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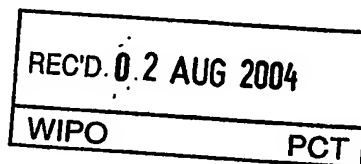
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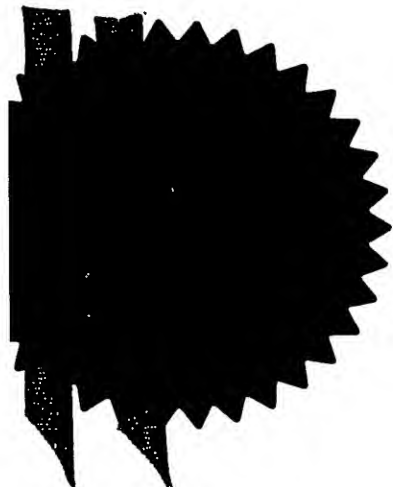


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*Andrew Giersey*

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3.	Full name, address and postcode of the or each applicant (underline all surnames)	The BOC Group plc Chertsey Road Windsorham Surrey GU20 6HJ		
	Patents ADP Number (if you know it)	797594900		
	If the applicant is a corporate body, give the country/state of its incorporation	Great Britain		
4.	Title of the invention	Coating		
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## 1 COATING

The present invention relates to a coating having a good resistance to aggressive and corrosive atmospheres generated by abrasive particles and halogen and inter-halogen gases (including their reactive species and corrosive compounds), such as chlorine, boron-trichloride, hydrogen bromide, fluorine and chlorine-trifluoride. More specifically but not exclusively, the invention relates to corrosion resistant coatings for use on machined parts, including precision machined parts, used as components in apparatus such as vacuum pumps, which are used in the manufacture of semi-conductors chips and are therefore susceptible to corrosion from the corrosive atmospheres referred to above. The invention also relates to metal and plastic substrates coated with the coating of the invention, methods of preventing or inhibiting the corrosion of such substrates as well as methods of forming the coating.

Vacuum pumps are used in the manufacture of semi-conductor chips to facilitate the control of the various environments that the chip must be exposed to during the various processes involved in the manufacture thereof. Such pumps are typically manufactured using cast iron and steel components, many of which are precision engineered to ensure optimum performance of the pump. Plastic based parts may also be used as components in vacuum pumps under certain conditions as described below.

25

Iron castings and steels have for a long time been used in the manufacture of component parts for equipment used in a wide range of industries, including the petro-chemical and semi-conductor industries. These parts are cheap, exhibit good thermal and thermo-mechanical properties and are relatively easy to form. However, in the semi-conductor industries the increasing use of high flow rates of the process gases (such as chlorine, boron-trichloride, hydrogen bromide, fluorine and chlorine-trifluoride) together with the associated elevated temperatures and pressures required have resulted in the severe corrosion of the iron

and steel component parts. Such corrosion leads to equipment failure, leakage of process chemicals and possible process contamination, and reduced process efficiency. Not to mention the huge costs associated with un-planned downtime.

5

In an attempt to minimise these problems, it has been common practice within many industries to passively protect many of component parts, since this represents a cheaper alternative to the more expensive active protection that is available. The use of aluminium coating on iron castings and steels, for example, has been used in a variety of industries to provide good corrosion and heat resistance (see, for example, *Carbon and Alloy Steels pp. 228-229, and Surface Engineering pp. 1155, both in Metal Handbook® Desk Edition, Second Edition, 1998. Edited by J.R. Davis. Prepared under direction of ASM International Handbook Committee.*). In addition, hot-sprayed ceramic coatings applied directly to the metal surface have also been used to protect iron and steel castings in abrasive and high temperature applications (see, for example, *Surface Engineering pp 1164-1165, in Metal Handbook® Desk Edition, Second Edition, 1998. Edited by J.R. Davis. Prepared under direction of ASM International Handbook Committee.*).

20

For component parts based on aluminium and its alloys, the use of a novel ceramic coating solution to provide corrosion resistance has been proposed. The process is described in EP 1,050,606; EP 0,545,230 and US 5,487,825 and involves the direct surface conversion of the aluminium substrate to give a sintered dense and hard ceramic coating that is atomically bound to the metal surface. The process can be used in the manufacture of precision-machined aluminium parts.

25

It has been proposed (JP 10219426) that corrosion resistance can be provided for a nickel-based alloy by forming an aluminium oxide ( $\text{Al}_2\text{O}_3$ ) layer on an aluminium coating applied thereto and which also has a diffusion layer within the nickel-based substrate. The formation of the diffusion layer necessitates heating the substrate at temperatures not less

30

than the melting point of aluminium, which leads to the distortion of the substrate. Such a process is clearly not suitable for the manufacture of precision-machined component parts.

5 It has also been suggested that such corrosion problems can be overcome by substituting the iron and steel parts with more expensive materials such as nickel rich iron base alloys, Monel, Inconel or higher nickel content alloys. However, these materials are expensive and do not represent a cost efficient alternative for use as component parts.

10

More recently there has been a move towards the use of plastic based component parts in a variety of industries in an attempt to replace the metal component parts traditionally used. The versatile nature of plastics means that they can be used to replace metal parts for a variety  
15 of reasons. Plastic parts can be manufactured by a variety of means and can be tailored to meet a number of application requirements. In addition their reduced weight and cost in comparison to metals means that they represent an attractive alternative in the manufacture of machine parts. However, because of the susceptibility of these materials to the  
20 Intensively corrosive, oxidative and aggressive environments encountered in the semi-conductor industry, their use in equipment in this industry has been limited. Most plastic materials will readily wear in the presence of abrasive particles and many hydrocarbon-based plastics may spontaneously combust in the presence of fluorine or oxygen gas.

25

Many attempts have been made to impart wear and corrosion resistance to a number of plastics materials, the provision of ceramic coatings being particularly popular. However, the application of ceramic coatings to plastic substrates has not always proved easy because, unlike  
30 metal surfaces, it is difficult to form ceramic coatings on plastic surfaces that exhibit good adherence and do not flake off in service. This is thought to be due to the non-conductive nature of the plastic surface, which results in the build up of electrostatic charge during the spraying process and acts to repel the sprayed ceramic particles.

Several potential solutions have been proposed to overcome this problem. One solution described in US patent no 3,179,531 is the incorporation of refractory materials intermixed into the top layer of the surface to be coated. The refractory material is firmly embedded in the top surface and provides a bonding surface for the refractory material which is subsequently sprayed thereover to the desired thickness. In US - 3,892,883 adherence is improved by utilising two intermediate layers - the first layer being copper/glass, which is adherent to the composite surface; and the second layer being a nickel aluminate, which bonds well to both the copper/glass layer and to the subsequent plasma-sprayed refractory layer. In US 4,388,373 an adherent intermediate layer is flame sprayed onto the plastic surface using a powder composition consisting of a mineral powder admixed with small amounts of nylon and epoxy powders. Further, in US 4,997,704 an adherent intermediate layer was first applied to the surface of the plastic using an adherent adhesive incorporating a substantial amount of conductive filler materials (eg metals or metalloids) to significantly lower the surface resistivity of the material prior to the deposition of ceramic particles using plasma-spraying techniques. In addition AU 2,396,601 describes the preparation of ceramic coated plastic substrates: the surface of the substrate to be coated is subjected to machining in order to generate residual compressive stress in the outer layers and hence, promote anchoring or mechanical locking when the ceramic powder is thereon sprayed using hot spraying techniques.

It should be noted that these processes involve the use of ceramic powders for coating. Because ceramics are non-conductive, the potential for repulsion of the sprayed particles by the electrostatic charges built-up on the polymer surface, (even using methods which improve the surface conductivity), will always exist, and there will always be doubts about the effectiveness of the processes and the integrity of ceramics coatings so produced. In addition the costs and cumbersome nature of the above-

mentioned methods mean that they are unsuitable in the manufacture of precision parts with tight tolerances

There is therefore a need for a corrosion resistant coating that can be easily applied to a metal or plastic substrate and which exhibits good adhesion thereto. The present invention addresses that need.

A first aspect of the invention provides an anti-corrosive coating for a metal or plastic substrate comprising a first layer of a barrier layer-forming metal or an alloy thereof applied directly or indirectly to the substrate and a second layer of a ceramic oxide of said barrier layer-forming metal or alloy thereof over said first layer.

By the term "anti-corrosive" it should be understood to mean that the coating is capable of withstanding wear and degradation as a result of exposure to abrasive particles and gases such as fluorine, chlorine-trifluoride, tungsten-hexafluoride, chlorine, boron-trichloride, hydrogen bromide, oxygen and the like.

By the term "barrier layer-forming metal" it should be understood to mean those metals and their alloys (such as Al, Mg, Ti, Ta, Zr, Nb, Hf, Sb, W, Mo, V, Bi), the surfaces of which naturally react with elements of the environment in which they are placed (such as oxygen) to form a coating layer, which further inhibits the reaction of the metal surface with said reactive environmental elements. The thickness of the barrier layer can be increased using techniques such as anodic-plasma oxidation (APO), anodic spark oxidation (ASO), electrolytic plasma oxidation (EPO), micro-arc oxidation (MAO) and plasma electrolytic ceramic oxide coating (PECOC), by anodically charging the metal layer and increasing the voltage. During the use of these techniques, a partial oxygen plasma forms at the metal/gas/electrolyte phase boundary and results in the creation of a ceramic oxide layer. The metal ion in the ceramic oxide layer is derived from the metal and the oxygen formed during the anodic reaction of the aqueous electrolyte at the metal surface. At temperatures



of 7000K associated with the formation of the plasma, the ceramic oxide exists in a molten state. This means that the molten ceramic oxide can achieve intimate contact with the metal surface at the metal/oxide boundary, which means that the molten ceramic oxide has sufficient time to contract and form a sintered ceramic oxide layer with few pores. At the electrolyte/oxide boundary, however, the molten ceramic oxide is quickly cooled by the electrolyte and the gases flowing away, notably oxygen and water vapour, leaving an oxide ceramic layer with increased porosity. Thus, the ceramic oxide layer so formed is itself characterised by three layers or regions. The first is a transitional layer between the metal and the coating where the metal surface has been transformed, resulting in excellent adhesion for the coating. The second is the functional layer, comprising a sintered ceramic oxide containing hard crystallites that give the coating its high hardness and wear resistance characteristics. The third is the surface layer, which has lower hardness and higher porosity than the functional layer

It will be appreciated from the foregoing that the ceramic oxide second layer is atomically bound to the underlying first layer and is formed from the surface of the barrier layer-forming metal or alloy thereof of the first layer. This means that the second ceramic oxide layer so produced exhibits greater adhesion to the underlying first layer than would be formed from an externally applied plasma sprayed ceramic second coat. The second ceramic oxide layer of the coating of the first aspect of the invention exhibits superior surface properties such as extreme hardness, very low wear, detonation and cavitation resistance, good corrosion and heat resistance, high dielectric strength and a low coefficient of friction. In addition, it is also resistant to corrosion from halogens, inter-halogen compounds and other semiconductor processing chemicals excited by plasma.

It will be appreciated that the resistant and highly adherent coatings of the first aspect of the invention can be used to protect

component parts formed from iron, steel and plastic substrates and which may be used in the corrosive environments described above.

5 From the foregoing it will be appreciated that the external surface of the sintered ceramic oxide layer of the second layer of the coating of the first aspect of the invention is in some applications characterised by a low porosity. In such situations out-gassing from the coated substrate material is minimised.

10 In other applications, the external surface of the second layer may be irregular and exhibit some porosity. In order to ensure extreme hardness, low wear and good corrosion resistance, the external surface of this second layer may be removed by grinding to expose the underlying sintered ceramic oxide layer, which provides the superior surface  
15 properties referred to above.

Alternatively, where the external surface of the second layer exhibits some porosity it can serve as a matrix for an optional third layer of a composite nature. In such situations, materials suitable for forming  
20 the third composite layer include a lubricant or paint, for example. It will be appreciated that the pore sizes of the external surface of the second layer are of a size that are capable of retaining the material of the third layer.

25 In one embodiment of the first aspect of the invention there is provided an anti-corrosive coating for a metal or plastic substrate comprising a first layer of a barrier layer forming metal or an alloy thereof formed directly or indirectly on the substrate; a second layer of a ceramic oxide of said metal or alloy thereof formed over said first layer and a third  
30 layer of a composite nature formed over the second layer. As indicated above, the third layer is suitably formed as a composite coating. Suitable examples of such composite coatings include lubricants such as fluorocarbons, poly-tetrafluoroethylene (PTFE), molybdenum disulfide ( $\text{MoS}_2$ ), graphite and the like or paint, which are retained by the porous

external surface of the second layer. The third layer is preferably formed directly over the second layer, the second layer providing a key for the adhesion of said third layer.

5 As indicated above, the coatings may be applied to a metal or plastic substrate to impart improved corrosion resistance thereto. A second aspect of the invention therefore provides a corrosion-protected substrate comprising a metal or plastic substrate having a coating according to the first aspect of the invention applied thereto.

10

The coatings of the first aspect of the invention can be readily and easily formed on both metal and plastic substrates and a third aspect of the invention provides a method of forming a coating according to the first aspect of the invention comprising the steps of forming a first layer of a  
15 barrier layer-forming metal or alloy thereof on said metal or plastic substrate and forming a second layer of a sintered ceramic oxide of said barrier layer forming metal or alloy thereof directly onto the surface of said first layer. It will be appreciated that the method of the third aspect of the invention can be used to form the corrosion protected metal and  
20 plastic substrates according to the second aspect of the invention.

The first layer is suitably applied by depositing a layer of the barrier layer-forming metal or alloy thereof directly or indirectly (depending on substrate) onto the substrate surface. The metal layers are preferably  
25 deposited onto the surface of the substrate using (i), sifting or compression of the powder or wrapping of the foil onto a liquid adhesive, after it has been applied to the surface or (ii), hot spraying techniques such as sputtering, plasma spraying, arc-spraying, flame spraying, vacuum-metallizing, high velocity oxyfuel spraying; combinations thereof  
30 and the like, which are well known to a skilled person. These methods ensure that the barrier forming metal or alloy thereof is both well adhered to and does not degrade the underlying substrate. Possible procedures for forming metal-ceramics composite coats on polymeric or metallic substrate have been described in US 4997704 and AU 2,396,601.

Whatever procedure or combination thereof adopted, the parameters must be adjusted to values suitable to obtain homogeneous coatings, with low porosity value and free of cast-in (embedded) particles, oxides and cracks that will compromise the formation of the sintered ceramic oxide coat by anodic-plasma oxidation.

As indicated above, the second layer is formed by anodic plasma oxidation of the surface of the metal layer or alloy thereof to form a sintered ceramic oxide layer. The ceramic layer is suitably formed by immersing an anodically charged metal coated part in an alkaline electrolyte (e.g., aqueous solution of an alkali metal hydroxide and sodium silicate) using the stainless steel bath acting as the counter electrode and applying an AC voltage in excess of 250V applied to the part. During the use of these techniques, a partial oxygen plasma forms at the metal/gas/electrolyte phase boundary and results in the creation of a ceramic oxide layer. The metal ion in the ceramic oxide layer is derived from the metal and the oxygen formed during the anodic reaction of the aqueous electrolyte at the metal surface. At temperatures of 7000K associated with the formation of the plasma, the ceramic oxide exists in a molten state. This means that the molten ceramic oxide can achieve intimate contact with the metal surface at the metal/oxide boundary, which means that the molten ceramic oxide has sufficient time to contract and form a sintered ceramic oxide layer with few pores. At the electrolyte/oxide boundary, however, the molten ceramic oxide is quickly cooled by the electrolyte and the gases flowing away, notably oxygen and water vapour, leaving an oxide ceramic layer with increased porosity. The bath temperature is maintained constant at about 20°C. A constant current density of at least 1A/dm<sup>2</sup> is maintained in the electrolytic bath until the voltage reaches a predetermined end value, consistent with the formation of an insulating layer. Under these conditions, one obtains typically about 1 micron of ceramic oxide coating per minute. Ceramic coating thickness up to about 100 micron can be obtained in 60 minutes, depending on barrier forming metal type and alloy. The processes have been described in EP 1,050,606; EP 0,545,230 and US 5,487,825. The

required current density to initiate the plasma process may be as high as 25A/dm<sup>2</sup> if the initially deposited barrier forming metal layer is rough and porous.

5 Preferred anodic-plasma oxidation processes for the formation of the second layer include micro-arc oxidation, anodic spark oxidation, electrolytic plasma oxidation, or plasma electrolytic oxidation and the like, which are well known to a person skilled in the art. Such processes have been described in EP 1,050,606; EP 0,545,230 and US 5,487,825.

10

The anodic-plasma oxidation is preferably carried out in a weak aqueous alkaline electrolyte of pH from 7.5 to 8, at temperatures about 20°C, which means that the integrity of the substrate material is little affected. As indicated above the melting that occurs during the formation  
15 of the ceramic coating or second layer tends to fill out any pores in the underlying barrier forming metal layer resulting in an impermeable interfacial region between the layers.

The external surface of the second layer may be irregular and  
20 exhibit some porosity in some applications. In order to further enhance its surface properties, a third layer of a composite material may optionally be formed over the second layer, the pores of said second layer retaining the new material. This third layer reduces the porosity of the surface of the second layer and further enhance the corrosion resistance thereof.  
25 Suitable coatings include any of the composite coatings referred to above, and when the pore sizes of said second layer allow, include nickel, chromium, molybdenum, tungsten and carbides thereof. The techniques used for forming said composite layers are well known to skilled person and generally involve the impregnation of the external surface of the  
30 second layer with another material, sometimes including a curing step, to give a composite coating with multiple properties. Such a process has been described in US 5,487,825

Alternatively, where the surface of the second layer exhibits some porosity, it may optionally be removed using techniques such as grinding, polishing, tumbling, rumbling and the like.

5        It will be appreciated that the method of the third aspect of the invention provides a simple and cost effective route to the provision of adherent and coherent ceramic coatings on both metal and plastic substrates and is also applicable to the manufacture of precision parts with tight tolerances.

10

For both metal and plastic substrates, the deposition of barrier layer-forming metal or alloys thereof on the surface of the substrate during the formation of the first layer has little effect on the bulk temperature of the substrate, thereby preventing distortion thereof. When  
15        employing the hot spraying techniques, the superior wetting properties of the molten metal particles on the substrate surface, when compared to conventionally sprayed ceramic particles, lead to the formation of a first layer having a low porosity.

20

In addition the ceramic coat obtained by anodic-plasma oxidation of the surface of the first layer is tightly bound to the underlying barrier layer-forming metal layer, because the surface of the metal layer is itself transformed to create a strong bond between the first and second layers. This means that the ceramic coat of the second layer exhibits greater  
25        adhesion than a layer formed by hot-spraying an externally applied ceramic coat.

30

Also, for plastic substrates the formation of the second ceramic oxide coating layer over the underlying barrier layer-forming metal layer overcomes the problems of electrostatic repulsion commonly encountered when depositing ceramic particles directly onto the surfaces of plastic substrates.

It will be appreciated that the method of the third aspect of the invention can be used to inhibit the corrosion of any metal or plastic substrates to which it is applied and a fourth aspect of the invention provides a method for preventing or inhibiting the corrosion of a metal or plastic substrate comprising the steps of applying the coating of the first aspect of the invention in accordance with the method of the third aspect of the invention.

As indicated above the coated substrates of the invention find particular application as component parts (including precision machined component parts in vacuum pumps) used in the manufacture of semiconductor wafers. A fifth aspect of the invention provides a corrosion resistant component for a vacuum pump comprising a metal or plastic substrate having formed thereon a coating according to the first aspect of the invention.

A sixth aspect of the invention provides a vacuum pump comprising one or more corrosion resistant components according to the second aspect of the invention.

The invention will now be described with reference to the following non-limiting examples. Variations on these falling within the scope of the invention will be apparent to a person skilled in the art.

## EXAMPLES

In the present invention, one can achieve adherent and coherent ceramic coating on iron castings, steels and plastics in a relatively simple and cost-effective manner that will also allow its application to precision parts with tight tolerances. The general method for achieving this is set out below, specific examples of which are presented thereafter.

(1.) Optional Initial treatment to roughen the surface of the substrate. Such methods may include Peening and Blasting; pickling and/or combinations thereof. For plastics, application of a thin layer of liquid adhesive, such as polyimides or epoxies, may follow the surface roughening.

(2.) Deposition of light barrier forming metals (e.g., Al, Ti, Mg, and their alloys) or composite (Al-Ni, Al-Cu, Al-Zn, Al-Mg, etc) onto the roughened surface (which may include a thin layer of liquid adhesive), using techniques such as sifting or compression of the metal powder or wrapping of the metal foil onto applied adhesive layer, vacuum-metallizing, sputtering, plasma-spraying, arc-spraying, flame-spraying, high-velocity-oxy-fuel-spraying, and combinations thereof. In the case of a plastic substrate, the most promising coating techniques are the compression of the metal powder or wrapping of the metal foil onto an applied liquid adhesive layer, the plasma spraying, the high velocity oxy-fuel spraying and combinations thereof, as these exhibit a low thermomechanical load with respect to other technologies. It will be appreciated that the above-mentioned spraying techniques have little thermomechanical impact on a metal substrate.

(3.) Anodic-plasma oxidation of the surface of the light barrier layer-forming metal layer to generate a sintered ceramic oxide layer, using techniques such as Micro-Arc-Oxidation (MAO), Anodic-Spark-Oxidation (ASO), Electrolytic-Plasma-Oxidation (EPO), and variants thereof. It is important that not all the first layer is converted to ceramic.

(4.) Optional finishing treatment of the surface of the ceramic coating layer using techniques such as keying in of substances ( $CF_x$ , fluorocarbons, PTFE,  $MoS_2$  and Graphite; Ni,



Cr, Mo, W and their Carbides; Paints and Resins), grinding, polishing, tumbling, rumbling, etc and combinations thereof.

**Example 1.**

**5 Preparation of Composite tubes coated with the process according to the invention**

A composite tube, manufactured in epoxy resin comprising carbon fibres (fibre direction to satisfy thermo-mechanical strain matching with  
10 metallic rotor parts), was subjected to the coating process according to the invention.

The surface of the composite tube was subjected to a low pressure grit blast using 60 mesh grit or light peening using bauxite. Thermal  
15 sandblasting may also be used. All methods serve to remove the sheen from the surface of the composite thereby to roughen the surface without damaging the fibres. The surfaces are then wiped with alcohol and dried to remove grease there-from.

20 The materials pre-selected for deposition by plasma spray, include pure aluminium and aluminium-nickel alloy (80/20) having powders of nominal size  $\sim 10 \mu\text{m}$ . It is important to note that use of standard powders with nominal dimension 45 - 90  $\mu\text{m}$  tend to give a more porous coat.

25 The powders were plasma sprayed onto the substrate surface using a standard Ar/H<sub>2</sub> plasma, nominally 40 kW power level. Either powder type resided about 0.1 ms in the plasma at  $\sim 15000^\circ\text{C}$ , before being projected onto the target substrate revolving at 60 rpm speed, at a distance of between 150 - 180 mm. The speed of the particles impinging  
30 on the substrate range from 225 m/s - 300 m/s, thus permitting splaying out (or wetting) of the molten particles and with some degree of penetration into the substrate. The average substrate temperature during the plasma spraying process remains in the range 100 - 150°C. The coating thickness is controlled by duration of the spraying, and

afterwards, the component is slowly cooled in still air. Then the surfaces were machined by grinding with a 180 SIC grinding wheel to remove the surface roughness, leaving a final ground coating thickness of about 50  $\mu\text{m}$

5

The metal layer obtained as described above is anodically-plasma oxidised in an electrolyte, (an aqueous solution of an alkali metal hydroxide and sodium silicate or sodium aluminate, or sodium metaphosphate), at a pH of 7.6. Using a current density of 12 A/dm<sup>2</sup>; an electrolyte temperature of 20 °C  $\pm$  3 °C, and a coating time of 60 minutes, a voltage end value of 350V is registered. The component with ceramic layer is washed and dried. The thickness of the ceramic layer is 30  $\mu\text{m}$ .

The corrosion resistance of the composite tube coated in this manner has four times better corrosion resistance than un-coated epoxy-carbon fibre composite tube in semiconductor applications. In particular it was found that IPX pumps that are coated with the ceramic lasted four times longer than un-coated pumps when exposed to 4500 litres each of Chlorine, Bromine and Fluorine.

Optionally, the ceramic coated component is immersed and moved within an aqueous anionic PTFE dispersion having a particle size  $\sim$  0.3  $\mu\text{m}$ , then washed under a flow of hot water (90 °C) and is dried with hot air. This enhances the corrosion resistance of the coating.

25

#### Example 2

#### Preparation of Composite tubes coated with the process according to the invention

30

A composite tube, manufactured in epoxy resin comprising carbon fibres (fibre direction to satisfy thermo-mechanical strain matching with metallic rotor parts), was subjected to the coating process according to the invention.

The surface of the composite tube was subjected to a low pressure grit blast using 60 mesh grit, an alternative is light peening using bauxite. Thermal sandblasting may also be used. All methods serve to remove the sheen from the surface of the composite thereby to roughen the surface without damaging the fibres. The surfaces were then wiped with alcohol and dried to remove grease there-from, prior to application of a thin liquid layer of epoxy adhesive. The adhesive was applied using a paintbrush.

The materials pre-selected for deposition by compression onto the liquid adhesive, include pure aluminium and aluminium-nickel alloy (80/20) having powders of nominal size  $\sim 10 \mu\text{m}$ . It is important to note that use of standard powders with nominal dimension 45 - 90  $\mu\text{m}$  tend to give a more porous coat.

By rolling compaction, over a bed of the metal powder, it was possible to compress the powders onto the surfaces of the tube. Cure of the adhesive was achieved by placing the powder-coated tube for 1 hour in an oven pre-set to  $120^\circ\text{C}$ . The coating has an inner layer where the metal powder is intermixed with the adhesive and an outer layer where the powder is keyed onto the inner layer. Then the surfaces were machined by grinding with a 180 SiC grinding wheel to remove the surface roughness, leaving a final ground coating thickness of about 30  $\mu\text{m}$ .

The metal layer obtained as described above was anodically-plasma oxidised in an electrolyte, (an aqueous solution of an alkali metal hydroxide and sodium silicate or sodium aluminate, or sodium metaphosphate), at a pH of 7.6. Using a current density of  $20 \text{ A/dm}^2$ ; an electrolyte temperature of  $20^\circ\text{C} \pm 3^\circ\text{C}$ , and a coating time of 75 minutes, a voltage end value of 400V is registered. The component with ceramic layer was washed and dried. The thickness of the ceramic layer was 10  $\mu\text{m}$ . The corrosion resistance of the composite tube coated in this manner has four times better corrosion resistance than un-coated epoxy-carbon fibre composite tube in semiconductor applications. In particular it was

found that IPX pumps that are coated with the ceramic lasted four times longer than un-coated pumps when exposed to 4500 litres each of Chlorine, Bromine and Fluorine.

- 5            Optionally, the ceramic coated component can be immersed and moved within an aqueous anionic PTFE dispersion having a particle size  $\sim 0.3 \mu\text{m}$ , then washed under a flow of hot water ( $90^\circ\text{C}$ ) and dried with hot air. This enhances the corrosion resistance of the coating.

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### **Example 3**

#### **Preparation of Composite tubes coated with the process according to the invention**

- 15            Samples from example 2 above, with the ground metal-coat layer only, were further subjected to plasma spray.

20            The materials pre-selected for deposition by plasma spray, included pure aluminium and aluminium-nickel alloy (80/20) having powders of nominal size  $\sim 10 \mu\text{m}$ . It is important to note that use of standard powders with nominal dimension  $45 - 90 \mu\text{m}$  tend to give a more porous coat.

- 25            The powders were plasma sprayed onto the metal-coat layer surface using a standard  $\text{Ar}/\text{H}_2$  plasma, nominally 40 kW power level. Either powder type resided about 0.1 ms in the plasma at  $\sim 15000^\circ\text{C}$ , before being projected onto the target substrate revolving at 60 rpm speed, at a distance of between 150 - 180 mm. The speed of the particles impinging on the substrate range from 225 m/s - 300 m/s, thus permitting splaying out (or wetting) of the molten particles and with some degree of penetration and bonding into the metal-coat layer. The average  
30            substrate temperature during the plasma spraying process remained in the range  $100 - 150^\circ\text{C}$ . The coating thickness was controlled by duration of the spraying, and afterwards, the component was slowly cooled in still air. Then the surfaces were machined by grinding with a 180 SIC grinding

wheel to remove the surface roughness, leaving a final ground coating thickness of about 60  $\mu\text{m}$

The metal layer obtained as described above was anodically-plasma  
5 oxidised in an electrolyte, (an aqueous solution of an alkali metal hydroxide and sodium silicate or sodium aluminate, or sodium metaphosphate), at a pH of 7.6. Using a current density of 12 A/dm<sup>2</sup>; an electrolyte temperature of 20 °C  $\pm$  3 °C, and a coating time of 60 minutes, a voltage end value of 350V was registered. The component with ceramic  
10 layer was washed and dried. The thickness of the ceramic layer was 40  $\mu\text{m}$ . The corrosion resistance of the composite tube coated in this manner has four times better corrosion resistance than un-coated epoxy-carbon fibre composite tube in semiconductor applications. In particular it was found that IPX pumps that are coated with the ceramic lasted four times  
15 longer than un-coated pumps when exposed to 4500 litres each of Chlorine, Bromine and Fluorine.

Optionally, the ceramic coated component may be immersed and moved within an aqueous anionic PTFE dispersion having a particle size ~  
20 0.3  $\mu\text{m}$ . then washed under a flow of hot water (90 °C) and dried with hot air. This enhances the corrosion resistance of the coating.

#### **Example 4**

#### **25 Preparation of Composite tubes coated with the process according to the invention**

A composite tube, manufactured in epoxy resin comprising carbon fibres (fibre direction to satisfy thermo-mechanical strain matching with  
30 metallic rotor parts), was subjected to the coating process according to the invention.

The surface of the composite tube was subjected to a low pressure grit blast using 60 mesh grit, an alternative is light peening using bauxite.

Thermal sandblasting may also be used. All methods serve to remove the sheen from the surface of the composite thereby to roughen the surface without damaging the fibres. The surfaces were then wiped with alcohol and dried to remove grease there-from, prior to application of a thin liquid layer of epoxy adhesive. The adhesive was applied using a paintbrush.

The material pre-selected for deposition by wrapping onto the liquid adhesive, is aluminium foil with a thickness of  $\sim 50 \mu\text{m}$ . Same material as used to wrap turkey for Christmas baking.

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The outer diameter of the tube was coated by press rolling the tube over a cut section of the foil, and with the excess trimmed off, leaving an overlap length of  $\sim 1 \text{ mm}$ . For the inner diameter, similar cut section of the foil was gently laid around the surface, followed by consolidation with a roller, and with the excess trimmed off, leaving an overlap length of  $\sim 1 \text{ mm}$ . Cure of the adhesive was achieved by placing the foil-coated tube for 1 hour in an oven pre-set to  $120^\circ\text{C}$ .

The metal layer obtained as described above was anodically-plasma oxidised in an electrolyte, (an aqueous solution of an alkali metal hydroxide and sodium silicate or sodium aluminate, or sodium metaphosphate), at a pH of 7.6. Using a current density of  $8 \text{ A/dm}^2$ ; an electrolyte temperature of  $20^\circ\text{C} \pm 3^\circ\text{C}$ , and a coating time of 45 minutes, a voltage end value of 300V was registered. The component with ceramic layer is washed and dried. The thickness of the ceramic layer is  $35 \mu\text{m}$ . The corrosion resistance of the composite tube coated in this manner has four times better corrosion resistance than un-coated epoxy-carbon fibre composite tube in semiconductor applications. In particular it was found that IPX pumps that are coated with the ceramic lasted four times longer than un-coated pumps when exposed to 4500 litres each of Chlorine, Bromine and Fluorine.

30

Optionally, the ceramic coated component may be immersed and moved within an aqueous anionic PTFE dispersion having a particle size  $\sim$

0.3  $\mu\text{m}$ . then washed under a flow of hot water (90 °C) and is dried with hot air. This enhances the corrosion resistance of the coating.

## 5 Example 5

### **Preparation of spheroidal graphite cast Iron (SG Iron) and Mild Steel coated with the process according to the invention**

A SG Iron sample, 100 mm x 100 mm x 5 mm, and a Mild Steel sample, 100 mm x 100 mm x 5 mm, were subjected to the coating process according to the invention.

The surface of the samples was roughened by sandblasting, followed by pickling in a 10% HF aqueous solution at room temperature, for 60 minutes. These were then washed and dried.

The materials pre-selected for deposition by plasma spray, include pure aluminium and aluminium-nickel alloy (80/20) powders of nominal size  $\sim 10 \mu\text{m}$ . It is important to note that use of standard powders with nominal dimension 45 - 90  $\mu\text{m}$  tend to give a more porous coat.

The powders were plasma sprayed onto the substrate surfaces using a standard Ar/H<sub>2</sub> plasma nominally 40 kW power level. Either powder type resided about 0.1 ms in the plasma at  $\sim 15000$  °C, before being projected onto the target substrate revolving at 60 rpm speed, at a distance of between 150 - 180 mm. The speed of the particles impinging on the substrate range from 225 m/s - 300 m/s, thus permitting splaying out of the molten particles and with some degree of penetration into the substrate. The average substrate temperature during the plasma spraying process remains in the range 100 - 150 °C. The coating thickness is controlled by duration of the spraying, and afterwards, the component is slowly cooled in still air. Then the surfaces were machined by grinding with a 180 SiC grinding wheel to remove the surface roughness, leaving a final ground coating thickness of about 50  $\mu\text{m}$ .

The metal layers obtained as described above are anodically-plasma oxidised in an electrolyte (an aqueous solution of an alkali metal hydroxide and sodium silicate or sodium aluminate, or sodium metaphosphate) with a pH of 7.6. Using a current density of  $\sim 8 \text{ A/dm}^2$ , an electrolyte temperature of  $20^\circ\text{C} \pm 3^\circ\text{C}$ , and a coating time of 60 minutes, a voltage end value of 300V is registered. The components with ceramic layer are washed and dried. The thickness of the ceramic layer is  $\sim 30 \mu\text{m}$ . SG Iron coated in this manner has four times better corrosion resistance than un-coated SG Iron, in semiconductor applications. In particular it was found that IPX pumps that are coated with the ceramic lasted four times longer than un-coated pumps when exposed to 4500 litres each of Chlorine, Bromine and Fluorine.

Optionally, the ceramic coated component may be immersed and moved within an aqueous anionic PTFE dispersion having a particle size  $\sim 0.3 \mu\text{m}$ , then washed under a flow of hot water ( $90^\circ\text{C}$ ) and dried with hot air. This enhances the corrosion resistance of the coating.



**CLAIMS**

- 5 1. An anti-corrosive coating for a metal or plastics material substrate comprising a first layer of a barrier layer-forming metal or an alloy thereof, the first layer being directly or indirectly adherent to the substrate and a second layer of a ceramic oxide of said metal or alloy thereof over said first layer.
- 10 2. An anti-corrosive coating according to claim 1, wherein the barrier layer-forming metal or alloy thereof is a metal or alloy the surface of which naturally reacts with elements of the environment in which it is placed.
- 15 3. An anti-corrosive coating according to claim 2, wherein the barrier layer-forming metal or alloy thereof is selected from aluminium, magnesium, titanium, tantalum, zirconium, niobium, hafnium, tin, tungsten, molybdenum, vanadium, antimony and bismuth and alloys thereof.
- 20 4. An anti-corrosive coating according to any one of the preceding claims, in which the substrate is iron based.
- 25 5. An anti-corrosive coating according to any one of claims 1 to 4, in which the substrate is an epoxy-carbon fibre composite or fibre reinforced plastic.
- 30 6. An anti-corrosive coating according to any one of the preceding claims, which further includes a third layer of a composite coating material, the third layer being directly adherent to said second layer thereby to reduce the porosity of the anti-corrosive coating.

- 5 7. An anti-corrosive coating according to claim 6 characterised in that the composite coating material includes one or more of the substances:  $\text{CF}_x$ , fluorocarbons, PTFE,  $\text{MoS}_2$  and Graphite; Ni, Cr, Mo, W and their Carbides; Paints and Resins.
- 10 8. A corrosion-protected substrate comprising a metal or plastic substrate having a first layer of a barrier layer-forming metal or an alloy thereof, the first layer being directly or indirectly adherent to the substrate and a second layer of a ceramic oxide of said light metal or alloy thereof over said first layer.
- 15 9. A corrosion-protected substrate according to claim 8, wherein the barrier layer-forming metal or alloy thereof is a metal or alloy the surface of which naturally reacts with elements of the environment in which it is placed.
- 20 10. A corrosion-protected substrate according to claim 9, wherein the barrier layer-forming metal or alloy thereof is selected from aluminium, magnesium, titanium, tantalum, zirconium, niobium, hafnium, tin, tungsten, molybdenum, vanadium, antimony and bismuth and alloys thereof.
- 25 11. A corrosion-protected substrate according to any one of claims 8 to 10, wherein the substrate is iron based.
- 30 12. A corrosion-protected substrate according to any one of claims 8 to 10, wherein the substrate is epoxy-carbon fibre composite or fibre reinforced plastic.
13. A corrosion-protected substrate according to any one of claims 8 to 12, which further includes a third layer of a composite coating material, the third layer being directly

adherent to said second layer thereby to reduce the porosity of the anti-corrosive coating.

- 5 14. A corrosion-protected substrate according to claim 13 characterised in that the composite coating material includes one or more of the substances:  $CF_x$ , fluorocarbons, PTFE,  $MoS_2$  and Graphite; Ni, Cr, Mo, W and their Carbides; Paints and Resins.
- 10 15. A method of forming a corrosion resistant coating on a metal or plastic substrate comprising the steps of applying a first layer of a barrier layer-forming metal or alloy thereof directly or indirectly to the metal or plastic substrate and forming a  
15 second layer of a sintered ceramic oxide of said light metal or alloy thereof directly onto the surface of said first layer.
- 20 16. A method for preventing or inhibiting the corrosion of a metal or plastic substrate comprising the steps of applying a first layer of a barrier layer-forming metal or alloy thereof directly or indirectly to the metal or plastic substrate and forming a  
25 second layer of a sintered ceramic oxide of said light metal or alloy thereof directly onto the surface of said first layer.
17. A corrosion resistant component for a vacuum pump  
25 comprising a metal or plastic substrate having formed thereon a coating according to any one of claims 1 to 7 or in accordance with a method of any one of claims 15 and 16.
- 30 18. A vacuum pump comprising one or more corrosion resistant components according to claim 17.

**ABSTRACT  
COATING**

8 An anti-corrosive coating for a metal or plastics material substrate is disclosed which comprises a first layer of a barrier layer-forming metal or an alloy thereof, the first layer being directly or indirectly adherent to the substrate and a second layer of a ceramic oxide of said metal or alloy thereof over said first layer. Methods for manufacture of and applications for the coatings are also disclosed.

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